

Application of the above all-steric proposal leads to the prediction that reduction of 4-*t*-butyl-2,2-dimethylcyclohexanone (**3**) should give more axial attack than its unmethylated analog **2** owing to the greater influence of the 2-axial methyl group over the influence of the 2-axial hydrogen. This prediction has been borne out (see Table I); the experimental result however is contrary to what would be predicted by product development control, since the 4-*t*-butyl-2,2-dimethylcyclohexanols give more axial OH at equilibrium than the 4-*t*-butylcyclohexanols.

In the preceding paragraphs the additions of small species to unhindered cyclohexanones have been shown to be governed by the axial substituents in positions 2 and 6. However as the size of the entering group becomes larger, more and more interactions with the 3 and 5 axial hydrogens are felt, favoring to a greater extent the equatorial (over the axial) attack on the unhindered ketone. For example, the axial introduction of a methyl group (from methylmagnesium iodide) on the unhindered 4-*t*-butylcyclohexanone would provoke in the transition state a 1a-CH<sub>3</sub>-3a-H interaction which causes an attack from the equatorial side of the carbonyl group to the extent of 50%.<sup>8,12</sup> It is noteworthy that the axial introduction of a hydride ion (from Li-AlH<sub>4</sub>) on the 3,3,5-trimethylcyclohexanone which would provoke in the transition state a 1a-H-3a-CH<sub>3</sub> interaction also leads to a mixture of isomeric alcohols containing approximately equal parts of each.<sup>13</sup>

Although it is recognized that any extensive generalization on the stereochemistry of the hydride reductions will have to take into account such factors as

(12) (a) B. Cross and G. H. Whitham, *J. Chem. Soc.*, 3892 (1960); (b) C. H. Depuy and R. W. King, *J. Am. Chem. Soc.*, **83**, 2743 (1961); (c) W. J. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962).

(13) E. L. Eliel and H. Haubenstein, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

solvent,<sup>14</sup> nature of the hydride,<sup>15</sup> electrostatic effects,<sup>16</sup> internal complexes, the influence of added Lewis acids,<sup>17</sup> and the temperature,<sup>18</sup> it seems possible to explain all the stereochemical results of the hydride reduction of cyclic ketones on the basis of steric factors only. Extension of the concepts developed above to the field of other additions to cyclic sp<sup>2</sup> carbon atoms could be made and would, for example, help to bring about an understanding of the stereochemical results reported by Greene<sup>19</sup> in the field of free radicals.

### Experimental

The reduction reported in Table I were carried out in tetrahydrofuran with hydrides from a commercial source or prepared *in situ*. The reaction times at room temperature were about 3.5 hr. The normalized percentages of the isomeric alcohols formed were estimated from vapor phase chromatograms using the peak height times half-width band method. These chromatograms were recorded on a Burrell K-2 apparatus. Except for the reduction products of the cyclohexanones **2** and **3**, the conditions used for chromatography were a 1.5-m. column of 20% glycerol on Kromat FB and temperatures from 110–120°. The cyclohexanones **2** and **3** were analyzed on a 2.5-m. column of 20% Carbowax 20M on Kromat FB at 160°.

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(16) D. M. S. Wheeler and M. Wheeler, *Chem. Ind. (London)*, 463 (1961).

(17) (a) J. C. Richer and E. L. Eliel, *J. Org. Chem.*, **26**, 972 (1961); (b) E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

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## 2:3-Benzo-1-silacycloalkenes. II. Improved Syntheses and Reactions

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The di-Grignard reagents of 3-(*o*-bromophenyl)propyl bromide and 2-(*o*-bromophenyl)ethyl bromide reacted with dichlorosilanes to give benzosilacycloalkenes. The six-membered ring compound, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, was readily brominated by *N*-bromosuccinimide to give the 4-derivative. This compound coupled when allowed to react with magnesium and was converted into the ketone, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one.

Previously we reported the preparation of some 2:3-benzo-1-silacycloalkenes by ring closure of (*o*-chlorophenyl)alkylsilanes with molten sodium in refluxing toluene.<sup>1</sup> A possible use of these compounds is as precursors to larger ring systems.<sup>1b</sup> An independent synthesis of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (**I**) was realized by allowing 3-(*o*-bromophenyl)propyl bromide to react with magnesium in an ether-tetrahydrofuran mixture and subsequently treating the organomagnesium compound with dichlorodiphenylsilane. Although the yield of **I** was low, the method of synthesis suggested the presence of an aralkyl di-Grignard reagent hitherto unknown.<sup>2</sup> This

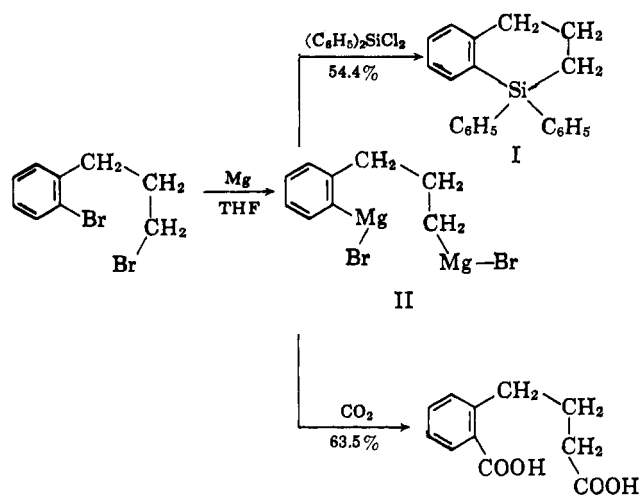
paper reports improved yields of the di-Grignard reagent, its reaction with carbon dioxide and dichlorosilanes, and some reactions of the resulting cyclic silanes.

When 3-(*o*-bromophenyl)propyl bromide was allowed to react with magnesium in tetrahydrofuran and the resulting organomagnesium compound was treated with dichlorodiphenylsilane, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (**I**) was obtained in a good yield. The di-Grignard reagent **II** was also characterized by carbonation to 4-(*o*-carboxyphenyl)butyric acid.<sup>3</sup> The di-Grignard compound also reacted with diphenyltin dichloride to give 2:3-benzo-1,1-diphenyl-1-stannacy-

(1) (a) H. Gilman and O. L. Marrs, *Chem. Ind. (London)*, 208 (1961); (b) *J. Org. Chem.*, **29**, 3175 (1964).

(2) I. T. Miller and H. Heaney, *Quart. Rev. (London)*, **11**, 109 (1957).

(3) P. D. Gardner, *J. Am. Chem. Soc.*, **78**, 3421 (1956). A sample of the acid was kindly furnished by Dr. Gardner.



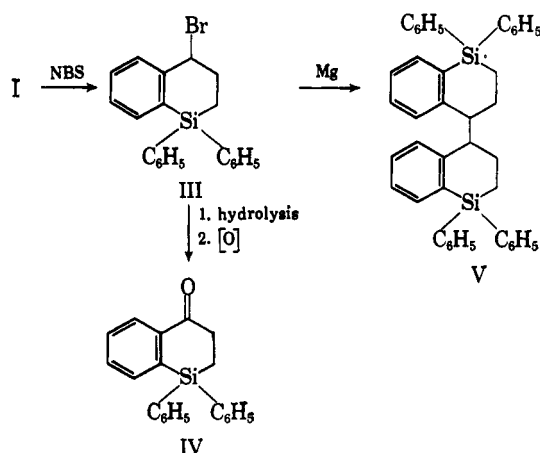
clohex-2-ene, and with methyldichlorosilane to afford the cyclic silicon hydride, 2:3-benzo-1-methyl-1-silacyclohex-2-ene. This compound was converted into the known 2:3-benzo-1-methyl-1-phenyl-1-silacyclohex-2-ene.

The actual composition of the di-Grignard II is probably not that shown. In view of the fact that magnesium bromide may be precipitated from Grignard solutions by the addition of dioxane, and the recent proposal<sup>4</sup> that Grignard reagents may better be represented by the complex  $\text{R}_2\text{Mg} \cdot \text{MgX}_2$ , II may have the following structure.



The five-membered ring homolog of I, 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene, was similarly prepared in good yield from 2-(*o*-bromophenyl)ethyl bromide. Therefore, the two di-Grignard reagents should be of general utility.

Since methods have now been developed for the synthesis of nonfunctional benzosilacycloalkenes, these compounds were converted into more useful functional derivatives. Treatment of I with *N*-bromosuccinimide gave 2:3-benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene (III). The bromo compound was then hydrolyzed



(4) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958). However, for further information on this topic, see R. E. Rundle and G. D. Stucky, *ibid.*, **85**, 1002 (1963), and references cited therein.

to the alcohol (crude) and subsequently oxidized to the ketone IV.

The structures of III and IV were based on elemental analysis, infrared and n.m.r. spectra, and their reactions. The infrared spectra of the two compounds contained three bands at 8.75–8.78, 8.91–8.93, and 9.03–9.05  $\mu$ , which are apparently characteristic of the six-membered benzosilacycloalkene nucleus.<sup>1b</sup> In the case of the ketone, a sharp carbonyl peak was present at 6.0  $\mu$ . The n.m.r. spectrum of III contained a single proton peak at  $\tau$  4.38, attributable to a tertiary benzylic hydrogen, and a multiplet of about 26 peaks at *ca.*  $\tau$  8, while that of IV showed two groups of signals of five peaks each with areas in the ratio of 1:1 centered at  $\tau$  7.19 and 8.56, typical of an  $\text{A}_2\text{B}_2$  system. Furthermore, of the n.m.r. spectra examined in the benzosilacycloalkene series,<sup>1b</sup> only IV contained a multiplet that was clearly shifted downfield from the rest of the aromatic protons. This shift was  $-0.44$  of a  $\tau$ -value. The multiplet, centered at  $\tau$  1.82 is assigned to the proton on the benzo portion that is *ortho* to the carbonyl group. Corio and Dailey<sup>5</sup> have observed similar downfield shifts for protons *ortho* to a carbonyl grouping. This *ortho* effect has been described as being due to diamagnetic anisotropy of the carbonyl group or to the incipient hydrogen bonding between the *ortho* proton and the substituent.<sup>6</sup> We observed that compound IV has properties different from those previously reported for this ketone (See Experimental).

Bromination of I with *N*-bromosuccinimide at the 5- or 6-position was excluded on the basis of the reactivity of III toward silver nitrate and further consideration of its n.m.r. spectrum. Compound III reacted rapidly with silver nitrate, a test characteristic of benzylic halides. Although halo groups  $\beta$  to a silicon atom are also reactive toward silver nitrate,<sup>7</sup> substitution at this position is incompatible with the n.m.r. spectrum of III.

In an attempt to prepare the Grignard reagent of III, which should serve as a useful synthetic intermediate, III was allowed to react with magnesium in tetrahydrofuran. Subsequent to hydrolysis the only isolable product was a compound melting at 271–273°, which, on the basis of its elemental analysis, molecular weight, and infrared spectrum, is believed to be 4,4'-bi-(2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene) (V). In a second run, the reaction mixture was carbonated. Again, the only product was V. Apparently, V is formed prior to hydrolysis or carbonation and probably results from a Wurtz-type coupling reaction enhanced by tetrahydrofuran.<sup>8</sup>

### Experimental<sup>9</sup>

2-(*o*-Bromophenyl)ethanol-1.—To a suspension of 11.4 g. (0.3 mole) of lithium aluminum hydride in 250 ml. of ether was added

(5) P. L. Corio and B. P. Dailey, *ibid.*, **78**, 3043 (1956).

(6) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 63.

(7) P. D. George, M. Prober, and J. R. Elliott, *Chem. Rev.*, **56**, 1065 (1956).

(8) H. Normant, "Advances in Organic Chemistry," R. A. Raphael, E. C. Taylor, and H. Wynberg, Eds., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 1–65.

(9) All melting and boiling points are uncorrected. Tetrahydrofuran was dried and purified by refluxing over sodium wire and then from lithium aluminum hydride immediately before use. The n.m.r. spectra were determined at 60 Mc. using tetramethylsilane as the internal standard.

dropwise to 47 g. (0.218 mole) of *o*-bromophenylacetic acid,<sup>10</sup> prepared by hydrolysis of *o*-bromobenzyl cyanide,<sup>11</sup> dissolved in 250 ml. of the same solvent. The mixture was refluxed for 30 min. and then treated with 20 ml. of ethyl acetate. The suspension was poured onto crushed ice and the organic layer was separated. The aqueous layer was extracted with ether and discarded. The combined organic layer was dried and concentrated. The residual oil was distilled to give 38.61 g. (88.1%) of colorless liquid, b.p. 130–132° (7.5 mm.),  $n_{20}^D$  1.5760,  $d_{20}^{20}$  1.4899.

*Anal.* Calcd. for  $C_8H_9BrO$ : C, 47.79; H, 4.51; MR, 45.01. Found: C, 47.95, 47.84; H, 4.56, 4.40; MR, 44.67.

The 1-naphthylcarbamate melted at 139.5–141° after recrystallization from ethanol.

**2-(*o*-Bromophenyl)ethyl Bromide.**—Phosphorus tribromide (21.66 g., 0.08 mole) was added to 33.85 g. (0.1684 mole) of 2-(*o*-bromophenyl)ethanol-1 cooled to ice-bath temperature. The mixture was warmed to room temperature and heated at 100° for 1 hr. After cooling and hydrolysis with water, ether was added and the layers were separated. The organic layer was dried over magnesium sulfate and the solvent was distilled. The concentrated oil was distilled under reduced pressure to give 34.4 g. (77.5%) of pure product, b.p. 113–115.5° (6 mm.),  $n_{20}^D$  1.5933,  $d_{20}^{20}$  1.7523.

*Anal.* Calcd. for  $C_8H_9Br_2$ : C, 36.40; H, 3.06; MR, 51.14. Found: C, 36.75, 36.86; H, 3.15, 3.13; MR, 51.07.

**3-(*o*-Bromophenyl)propanol-1.**—The alcohol was prepared in yields of 53 and 57% from the Grignard reagent of *o*-bromobenzyl bromide and ethylene oxide according to the method of Beeby and Mann,<sup>12</sup> b.p. 115–117° (0.8 mm.),  $n_{20}^D$  1.5699.

**3-(*o*-Bromophenyl)propyl Bromide.**—3-(*o*-Bromophenyl)propanol-1 was converted into the bromide by heating with phosphorus tribromide as described above for the ethyl derivative in yields of 78.8 and 78.2%, b.p. 128–129° (1.3 mm.),  $n_{20}^D$  1.5830,  $d_{20}^{20}$  1.668, lit.<sup>12</sup> b.p. 84–85° (0.3 mm.).

*Anal.* Calcd. for  $C_9H_{10}Br_2$ : C, 38.88; H, 3.63; MR, 55.62. Found: C, 39.57, 39.38; H, 3.80, 3.75; MR, 55.69.

**4-(*o*-Carboxyphenyl)butyric Acid.**—Five milliliters of a solution of 3-(*o*-bromophenyl)propyl bromide (6.95 g., 0.025 mole) in 95 ml. of tetrahydrofuran was added to 1.44 g. (0.06 g.-atom) of magnesium in 5 ml. of the same solvent. When the exothermic reaction began, the addition was completed over a 1.5-hr. period. The mixture was stirred for 3 hr. at room temperature and then heated gently for 1 hr. The yield of the di-Grignard reagent, determined by titration of an aliquot, was 76%. The mixture was carbonated by pouring jetwise onto a slurry of Dry Ice and ether. Subsequent to acid hydrolysis, the aqueous layer was separated, extracted with ether, and discarded. The combined organic layer was extracted with 200 ml. of a 5% sodium hydroxide solution and the extracts were acidified with concentrated hydrochloric acid. Filtration gave 4.02 g. of impure acid, m.p. 128–132°. Recrystallization from an ethyl acetate–heptane mixture afforded 2.65 g. (63.5%) of pure acid, m.p. 138–139°. The melting point was not depressed when admixed with a sample of the acid prepared by a different route.<sup>3</sup> Also, the infrared spectra were superimposable.

**2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene (I).**—The di-Grignard reagent of 3-(*o*-bromophenyl)propyl bromide was prepared in an 82% yield by adding 5.56 g. (0.02 mole) of the bromide in 85 ml. of tetrahydrofuran to 1.2 g. (0.05 g.-atom) of magnesium in 5 ml. of tetrahydrofuran and stirring the mixture for 18 hr. at room temperature, followed by 1.5 hr. at reflux. The filtered organomagnesium compound was added to 3.87 g. (0.0153 mole) of dichlorodiphenylsilane dissolved in 10 ml. of tetrahydrofuran. Color Test I<sup>3</sup> was negative after 1 hr. at reflux. Hydrolysis was effected by pouring into an aqueous ammonium chloride solution. Ether was added and the layers were separated. The aqueous layer was extracted thoroughly with ether and discarded. The combined organic layer was dried and the solvents were distilled. The residual material was treated with petroleum ether (b.p. 60–70°) to give 0.71 g. (21.5%) of diphenyl silanediol, m.p. and m.m.p. 154–156°.

The petroleum ether filtrate was concentrated and ethanol was added to the oil. The solid was filtered to afford 3.66 g. of impure product, m.p. 70–74°. Recrystallization from 95% ethanol gave 2.29 g. (54.4%) of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene,

m.p. 78–79.5°, identified by mixture melting point with an authentic sample<sup>1</sup> and by comparison of the infrared spectra.

**2:3-Benzo-1-methyl-1-silacyclohex-2-ene.**—A tetrahydrofuran solution (50 ml.) containing 6.79 g. (0.059 mole) of methylchlorosilane was treated with 0.059 mole of the di-Grignard reagent of 3-(*o*-bromophenyl)propyl bromide. After refluxing the mixture overnight, Color Test I was negative. Hydrolysis and the usual work-up gave an oil which was taken up in petroleum ether (b.p. 60–70°) and passed through a column of alumina. The petroleum ether eluate was distilled to give 3.13 g. (33.3%) of product, b.p. 106–106.5° (21 mm.),  $n_{20}^D$  1.5442.

*Anal.* Calcd. for  $C_{10}H_{14}Si$ : C, 73.99; H, 8.69. Found: C, 74.53, 74.62; H, 8.60, 8.63.

A portion (2.01 g., 0.0124 mole) of the cyclic silicon hydride was allowed to react with an excess of phenyllithium at reflux for 1 hr. After hydrolysis, the ether layer was dried and distilled. The concentrated oil was distilled under reduced pressure to give 1.95 g. (66.2%) of 2:3-benzo-1-methyl-1-phenyl-1-silacyclohex-2-ene, b.p. 93–94° (0.005 mm.). The infrared spectrum of the product was superimposable with that obtained by ring closure of [3-(*o*-chlorophenyl)propyl]methylphenylsilane with sodium.<sup>1b</sup>

**2:3-Benzo-1,1-diphenyl-1-stannacyclohex-2-ene.**—To a solution of diphenyltin dichloride (5.64 g., 0.0164 mole) in 10 ml. of tetrahydrofuran was added 0.0164 mole of the di-Grignard reagent of 3-(*o*-bromophenyl)propyl bromide in 85 ml. of the same solvent. Color Test I was negative after 2 hr. at reflux. The reaction mixture was hydrolyzed with an ammonium chloride solution and worked up in the usual manner. Chromatography of the reaction products over alumina using petroleum ether (b.p. 60–70°) as the eluent gave 600 mg. (9.4%) of colorless crystals, m.p. 70–71°. Recrystallization from ethanol did not alter the melting point.

*Anal.* Calcd. for  $C_{21}H_{26}Sn$ : C, 64.50; H, 5.15. Found: C, 64.65, 64.45; H, 5.43, 5.23.

Further elution of the column with benzene and ethyl acetate gave 2.0 g. of an oil which could not be purified further.

**2:3-Benzo-1,1-diphenyl-1-silacyclopent-2-ene.**—To 2.4 g. (0.1 g.-atom) of magnesium in 5 ml. of tetrahydrofuran was added dropwise a solution of 5.28 g. (0.02 mole) of 2-(*o*-bromophenyl)ethyl bromide dissolved in 85 ml. of tetrahydrofuran. Reaction started immediately and the addition was completed over a 1-hr. period. The mixture was stirred for 18 hr. at room temperature and then refluxed for 1 hr. The yield of the di-Grignard reagent (determined by the titration of an aliquot) was 75%. The solution was added to 3.8 g. (0.015 mole) of dichlorodiphenylsilane, and the reaction mixture was refluxed for 1 hr. Color Test I was negative. Subsequent to hydrolysis, the aqueous layer was separated, extracted with ether, and discarded. The combined organic layer was dried and the solvents were evaporated. Addition of petroleum ether to the residual oil gave 0.55 g. (17%) of diphenylsilanediol, m.p. and m.m.p. 146–148°. The filtrate was concentrated and the oily residue was treated with ethanol. Filtration gave 2.21 g. (51.5%) of colorless crystals, m.p. 61–63°. The solid was identified as 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene by mixture melting point and by comparison of the infrared spectra.<sup>1</sup>

**2:3-Benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene (III).**—A mixture of *N*-bromosuccinimide (5.92 g., 0.033 mole), 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (10.0 g., 0.033 mole), and benzoyl peroxide (0.1 g.) in 200 ml. of carbon tetrachloride was heated at reflux for 2.5 hr. Filtration of the cold suspension gave 3.04 g. (92%) of succinimide (mixture melting point). The carbon tetrachloride was removed with the aid of a water aspirator, and petroleum ether (b.p. 60–70°) was added to the residue. Slightly impure product (12.4 g.) was obtained by allowing the solution to stand for 3 days at 0°. Two recrystallizations from petroleum ether gave 9.5 g. (76%) of pure product, m.p. 95–97°.

*Anal.* Calcd. for  $C_{21}H_{19}BrSi$ : Si, 7.44. Found: Si, 7.35, 7.39.

The n.m.r. spectrum of the compound in deuterated chloroform supported the assigned structure, showing a closely coupled proton peak centered at  $\tau$  4.38, attributable to the tertiary benzylic proton, and a multiplet centered at about 8.0 for the remaining protons.

The bromo compound reacted rapidly with an ethanolic solution of silver nitrate.

**2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one (IV).**—To the bromo compound III (9.0 g., 0.0237 mole) dissolved in 250 ml. of acetone, 50 ml. of benzene, and 50 ml. of water was added

(10) P. P. Bedson, *J. Chem. Soc.*, **37**, 90 (1880).

(11) St. Opolski, L. Czaporowski, and J. Zacharoki, *Ber.*, **49**, 2283 (1916).

(12) M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 411 (1951).

(13) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

4.34 g. (0.026 mole) of silver acetate. The reaction flask was wrapped with aluminum foil and the mixture was stirred for 18 hr. at room temperature. The silver bromide was filtered and the filtrate was concentrated to about 40 ml. Ether was added and the layers were separated. The organic layer was dried ( $\text{MgSO}_4$ ) and evaporated. Attempts to induce crystallization failed.

The viscous oil (8.9 g.) was dissolved in 10 ml. of ether and treated with a solution of 1.75 ml. of concentrated sulfuric acid and 2.37 g. of sodium dichromate dihydrate made up to 15 ml. with water according to the method of Brown and Garg.<sup>14</sup> The reaction temperature was maintained at 7–10° during the addition of the dichromate solution (20 min.). After stirring for 1 hr. between 10 and 20°, ether was added and the mixture was diluted with water. The aqueous layer was separated, extracted with 2–50-ml. portions of ether, and discarded. The combined organic layer was washed with a sodium bicarbonate solution and then with water. The ethereal solution was dried over magnesium sulfate and evaporated. Petroleum ether (b.p. 60–70°) was added to the residue and the crystalline product was collected by filtration, 4.45 g. (59.7%), m.p. 111–112° after recrystallization from a benzene–petroleum ether mixture.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{18}\text{OSi}$ : C, 80.21; H, 5.77; Si, 8.93. Found: C, 80.13, 80.37; H, 5.71, 5.84; Si, 9.05, 9.14.

The infrared spectrum of the compound in carbon disulfide contained prominent bands at 3.3, 3.45, and 6.0, 9.0, and 13.07  $\mu$ , indicative of aromatic and aliphatic C–H, carbonyl group, the silicon–phenyl linkage, and *ortho* disubstitution, respectively. The n.m.r. spectrum of the ketone as a carbon tetrachloride solution showed two multiplets of five peaks each centered at  $\tau$  7.19 and 8.56, representing the protons at the 5-position ( $\alpha$  to the carbonyl group) and 6-position, respectively, and two other multiplets at  $\tau$  1.82 and 2.26 for the aromatic proton on the benzo portion *ortho* to the carbonyl group<sup>5</sup> and the remainder of the aromatic protons.

Treatment of the ketone with an ethanolic solution of 2,4-dinitrophenylhydrazine gave the hydrazone as bright red flakes, m.p. 228–230° after recrystallization from ethyl acetate.

*Anal.* Calcd. for  $\text{C}_{27}\text{H}_{22}\text{N}_4\text{O}_4\text{Si}$ : C, 65.57; H, 4.49; N, 11.33. Found: C, 65.55, 65.72; H, 4.43, 4.57; N, 11.29, 11.26.

The reported<sup>15</sup> melting points of the ketone and hydrazone are 127 and 240° dec., respectively. The melting point of each derivative was depressed when admixed with those above. The infrared spectra of the two ketones were quite different. That of the previously prepared sample<sup>15</sup> contained medium to strong bands at 7.47, 8.20, 8.53, 9.28–9.62 (broad), and 12.33  $\mu$ , which were not present in the spectrum of the ketone prepared in this

(14) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(15) D. Wittenberg, P. B. Talukdar, and H. Gilman, *ibid.*, **82**, 3608 (1960).

investigation. The broad band at 9.28–9.62  $\mu$  may be attributed to the presence of an Si–O–Si or Si–O–C linkage.<sup>16</sup> The infrared spectra of the two hydrazones were similar, but not superimposable.

**Reaction of 2:3-Benzo-4-bromo-1,1-diphenyl-1-silacyclohex-2-ene with Magnesium.** Run 1.—A solution of 1.0 g. (0.00263 mole) of the bromo compound in 15 ml. of tetrahydrofuran was added dropwise to 0.1 g. (0.004 g.-atom) of magnesium and a crystal of iodine in 5 ml. of the same solvent. A reaction started immediately and, subsequent to complete addition, the mixture was refluxed for 2 hr. The reaction mixture was poured through a glass-wool plug into an ammonium chloride solution. Ether was added, the layers were separated, and the aqueous layer was extracted with ether. The combined organic layer was filtered to give 0.25 g. of a solid melting at 268–271°. The filtrate was dried and concentrated. An additional 0.11 g. of the high-melting solid was isolated. Further concentration of the filtrate gave a viscous yellow oil which could not be purified further.

The two solid fractions were combined and recrystallized from a benzene–petroleum ether (b.p. 60–70°) mixture to give 0.31 g. (39.2%) of fine needles, m.p. 271–273°. The infrared spectrum was similar to that of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, showing absorption bands at 3.28, 3.44, 9.05, and 13.28  $\mu$ , characteristic of aromatic and aliphatic C–H, the silicon–phenyl linkage, and *ortho* disubstitution, respectively. The compound has been assigned the structure 4,4'-bi(2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene) (V).

*Anal.* Calcd. for  $\text{C}_{42}\text{H}_{38}\text{Si}_2$ : C, 84.23; H, 6.39; Si, 9.38; mol. wt., 599. Found: C, 84.61, 84.40; H, 6.43, 6.35; Si, 9.25; mol. wt. (benzene), 580.

Run 2.—The bromo compound (1.15 g., 0.00303 mole) was allowed to react with 0.1 g. (0.004 g.-atom) of magnesium in 20 ml. of tetrahydrofuran as described above, except that the mixture was refluxed for 1 hr. and then carbonated. No acidic products were produced. From the organic layer, there was obtained 0.22 g. (24.2%) of the solid isolated in run 1, m.p. 270–273°, and a viscous oil.

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## Oxidations with Oxygen Difluoride. II. Addition to Unsaturated Carbon

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Controlled oxidative fluorination of selected olefins and acetylenes has been demonstrated. Direct preparation of  $\alpha$ -fluoro ketones, fluorohydrins, and  $\alpha,\alpha$ -difluoro ketones has been effected.

Following the initial preparation of oxygen difluoride ( $\text{OF}_2$ ) by Lebeau and Damiens<sup>1</sup> in 1927, the investigation of the chemistry of this powerful oxidant was confined to various inorganic systems.<sup>2</sup> However, recent work<sup>3</sup> has shown that  $\text{OF}_2$  oxidations of organic substrates can be controlled in the case of primary aliphatic amines. The facile amine oxidation,<sup>3</sup> which was rapid at  $-78^\circ$ , suggested extension of similar

techniques to study other Lewis base- $\text{OF}_2$  interactions.

It was found that certain olefins were sufficiently unreactive at  $-78^\circ$  and controlled addition could be achieved. Acetylenes, however, were slightly less reactive at  $-78^\circ$  and uptake of  $\text{OF}_2$  proceeded at a convenient rate at  $-40^\circ$ . In both cases, the products isolated contained a fluorine  $\alpha$  to an oxygen atom, e.g.,  $\alpha$ -fluoro ketones,  $\alpha,\alpha$ -difluoro ketones, and a fluorohydrin. Such products suggest direct addition of the elements of  $\text{OF}_2$  across the double or triple bond followed by further reaction (decomposition) leading to observed compounds. Such direct addition of  $\text{OF}_2$

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(2) See J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, part I, Longmans, Green and Co., New York, N. Y., for a complete survey.

(3) R. F. Merritt and J. K. Ruff, *J. Am. Chem. Soc.*, **86**, 1392 (1964).